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Effect of temperature and pressure on characteristics and reactivity of biomass-derived chars

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HIGHLIGHTS

- The effect of pressure on chars produced at low pyrolysis temperatures was studied.
- Special attention was devoted to the oxidation reactivity of the produced chars.
- Pyrolysis conditions and secondary char formation affected char porosity/reactivity.
- Secondary char formation becomes more important with pyrolysis temperature/pressure.
- The temperature interval 350–450 °C may be key in the tar repolymerization process.

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ABSTRACT

This study evaluates the influence of pyrolysis temperature (350–450 °C) and pressure (0.1–2.0 MPa) on product yields and char properties. Spruce chars were produced under slow pyrolysis conditions in a fixed bed reactor. Special attention was devoted to the study of the oxidation reactivity of the produced chars, and its relationship with the evaluated char properties. The obtained results showed that the effect of the pyrolysis condition on char production and in particular on the mechanism of secondary char formation strongly influenced the char reactivity. Additionally it has been observed that the interval of temperature between 350 and 450 °C may be key in the mechanism of tar repolymerization. The information provided in this study is of great interest for the determination of optimal operation conditions and the design of new gasification concepts or the development of bioenergy carriers via pyrolysis technologies.

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1. Introduction

Biomass is considered a renewable energy source with high potential to contribute to the growing needs for sustained energy supply, offering advantages such as (Brewer and Brown, 2012; EREC, 2010): (i) it is a widespread resource, (ii) reduces greenhouse emissions, (iii) brings about an increment in rural incomes and restoration of degraded lands, and (iv) represents an economical option versus oil and coal. However, the production of bioenergy on a large-scale still faces some barriers. These drawbacks are related to the geographical dispersion of biomass resources and to its moderate energy density, high oxygen content, hydrophilic properties and water content (van der Stelt et al., 2011), resulting in high transportation costs and technical difficulties for the biomass conversion processes to operate optimally. A possible approach to reduce the impact of these factors is to apply a thermal pretreatment to biomass (torrefaction/pyrolysis) in order to produce a carbonaceous solid product, commonly referred to as torrified biomass or char. This product presents higher energy density than biomass and very low moisture and hydrophilicity, and can be transported and stored more efficiently to be used in different energy applications (e.g. gasification). Although nowadays combustion is the dominant process, gasification is more efficient for power production and expands the versatility of biomass through the production of syngas for the synthesis of second generation biofuels (SNG, FT liquids, methanol, dimethylether, etc.) (Asadullah et al., 2003). According to these assumptions, within the next years the development of bioenergy carriers and the implementation of large-scale biomass technologies are expected.

Mild pyrolysis is one of the thermal pretreatments that are commonly applied in order to improve biomass properties as solid fuel. During pyrolysis, biomass is subjected to temperatures above 300 °C (typically in the range from 300 to 650 °C), in absence of oxidizing agent. The yields and properties of the different pyrolysis products strongly depend on the operating conditions and reactor

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configuration (Berrueco et al., 2014a; Cetin et al., 2004; Cordella et al., 2013; Kandiyoti et al., 2006; Manyà, 2012; Neves et al., 2011).

In order to optimize char production it is necessary to carefully select the conditions to be used in the pyrolysis process. The biomass pyrolysis step should ideally aim to give high yield of char with high reactivity. However, the process conditions needed for increasing char yield tend to decrease its reactivity. In order to obtain high char yields, tar release must be minimized, and this is achieved through promoting repolymerization reactions. However, repolymerization reactions produce stable and non-porous char deposits, which present poor gasification properties (Kandiyoti et al., 2006; Berrueco et al., 2014a). The main operating parameters governing the characteristics of the chars (as well as the other pyrolysis products) for a given type of biomass are temperature, heating rate, particle size, pressure, reaction time and the configuration of sample and reactor (Antal and Grønli, 2003; Berrueco et al., 2014a; Cetin et al., 2004; Cordella et al., 2013; Kandiyoti et al., 2006; Manyà, 2012; Neves et al., 2011). The pyrolysis problem at hand (i.e. enhancement of char formation during the pyrolysis process) may best be studied in a fixed bed reactor. This reactor configuration enables the operation at conditions that would tend to maximize the char yield, i.e. high pressures, relatively low heating rates and varying bed depths, which can be used to maximize the interaction between the evolving tars and the solids.

In this study the influence of pyrolysis temperature (350–450 °C) and pressure (0.1–2.0 MPa) on the product yields and char properties was evaluated. Spruce wood pyrolysis was investigated under slow heating rate (10 °C min^{-1}) in a fixed bed reactor. Special attention was paid to the chemical and physical characterization of the chars and the relation between composition and structure of the chars and their oxidation reactivity. The data provided will be of relevance for future pyrolysis studies and the design of new gasification concepts to enable a clean conversion of solid fuels into high-quality products.

2. Methods

2.1. Biomass preparation and characterization

Wood spruce sieved to a particle size range of 250–500 μm was used as biomass sample. The proximate and ultimate analyses of the samples were carried out using a LECO Thermogravimetric analyzer (TGA 701) and a LECO TruSpec CHN-S-O analyzer, respectively. The proximate analysis was conducted following the standard method ASTM D7582 for moisture, volatile matter and fixed carbon determination. The lower heating value was determined in an isoperibolic LECO Automatic calorimetric bomb (AC 600), according to the ASTM D5865-07 standard test method. Halogens (HCl, HF, HBr) and phosphorous (H_3PO_4) were recovered by washing the calorimetric bomb with Milli-Q water and quantified by ionic chromatography (DIONEX ACS 1100) according to the EN-15408:2011 standard method. The results of the biomass analyses appear gathered in Table 1. These data will be useful to assess the variations between the raw and pyrolyzed feedstock.

2.2. Setup and procedure for pyrolysis experiments

Pyrolysis experiments were performed in a laboratory-scale fixed bed reactor (PID Eng & Tech, Spain) made of stainless steel (305 mm in length and 13 mm i.d.). Temperature was measured by a thermocouple placed inside the biomass bed. The reactor was settled in a hot box and externally heated by a radiant furnace. The gas flowed downstream across the reactor and, after leaving the reaction zone, went through a cold trap and a coalescing filter, to retain condensable liquids. The cold trap, packed with stainless steel mesh, was cooled with a mixture of ice and water. Finally, the pyrolytic gas was collected in a Tedlar gas-sampling bag to be analyzed after the experiment. The gas composition and flow rate were measured by means of an online micro GC (Agilent 490) and a Bronkhorst High-Tech flowmeter, respectively.

2.2.1. Experimental procedure

The biomass samples weighting approximately 1.5 g were held on a porous plate placed inside the reactor. Prior to the beginning of the experiment, nitrogen (Praxair, Inc.) was forced through the reactor at atmospheric pressure during a period of 30 min to remove any presence of oxygen and guarantee a non-oxidative environment.

After the purging period, the nitrogen flow was set at 50 NmL min^{-1} (experiment flow conditions), and the system was pressurized to the desired value. When the target pressure was reached, the reactor was heated at 10 °C min^{-1} and the final temperature was held for 15 min. The gas collection bag was then detached from the system and the gas composition was analyzed in the micro GC. The reactor was cooled down under pressure, the nitrogen flow stopped and the solid and liquid products recovered and weighted. Specifically, tar was recovered by washing the reactor, downstream pipes and the cold trap with acetone. The solvent was then removed by purging with N_2 at room temperature until the tar was totally dry.

2.3. Gas and char analyses

An online micro GC (Agilent 490) was used to quantify the composition of the gas collected in the gas-sampling bag during the experiments. The chromatograph configuration includes three different channels that analyze the permanent gases (H_2, O_2, N_2, CO, CO_2 and CH_4) and hydrocarbons up to C_5. Further details can be found elsewhere (Berrueco et al., 2014b).

The proximate and ultimate analyses of the recovered chars were carried out following the same procedure cited above for the biomass sample characterization.

The char morphology was studied using a scanning electron microscope SEM (JEOL JSM 6400). Samples were mounted on a cylindrical aluminium stub (10 mm o.d., 10 mm high) glued to a carbon tab and then gold-coated under vacuum for 3 min with a Sputter Coater (Emitech K575X).

The pore structure and total surface area of each char sample were determined through CO_2 adsorption at 0 °C using a Quantachrome Autosorb-iQ-C sorption analyzer. All char samples were degassed in vacuum (10^{-5} Torr) at 300 °C during at least 3 h prior to analysis. Surface areas and pore size distributions of the chars were calculated using the Dubinin–Radushkevich (DR) equation.

2.4. Reactivity analysis

Char samples were analyzed to establish their reactivity at low temperatures in an O_2–N_2 atmosphere. Oxidation reactivity analyses were conducted in a Mettler Toledo TGA/DSC 1 microbalance equipped with a 34-positions sample robot. The produced biomass chars were ground and sieved to a particle size of 100–106 μm. The samples (about 1.5 mg) were evenly distributed in the crucibles (Al_2O_3 crucibles, 70 μl) as a very thin layer. During the analyses the chars were heated under nitrogen atmosphere at a constant heating rate of 20 °C min^{-1} up to the analysis temperature, followed by a 5 min period for temperature stabilization. After this period the atmosphere was switched to an O_2 (5 vol.%)–N_2 mixture and the analyses were performed under isothermal conditions at 320, 350 and 450 °C. All the analyses were carried out at

Table 1
Composition and heating value of the biomass feedstock (as received basis).

		Wood spruce
Proximate analysis (wt.%)	Moisture	5.03 ± 0.01
	Volatiles	77.2 ± 0.1
	Fixed carbon	17.5 ± 0.1
	Ash	0.36 ± 0.02
Ultimate analysis (wt.%)	C	47.2 ± 0.2
	H	6.21 ± 0.10
	O	46.2 ± 0.3
	N	0.02 ± 0.02
	S	0.03 ± 0.002
	F	>0.0015
	Cl	0.0021 ± 0.0001
	P	0.0018 ± 0.0007
Lower heating value (MJ/kg)	LHV	17.74 ± 0.09

atmospheric pressure, and the flow of nitrogen and O_2–N_2 mixture was set at 20 NmL min^{-1}.

3. Results and discussion

Spruce wood pyrolysis experiments were conducted at temperatures of 350 and 450 °C, and pressures of 0.1, 1.0 and 2.0 MPa. The experimental conditions and the main product yields of the experiments are shown in Table 2**.**

3.1. Pyrolysis yields

3.1.1. Product yields

Table 2 compiles the yields of the coproducts from the pyrolysis experiments. The main components were permanent gas, biomass char and a liquid fraction, which included water and tar. The shown values are the average of replicate experiments performed at each operating condition.

The gas yield decreased with the increment of pyrolysis pressure for both temperatures. In the pressure range from 0.1 to 1.0 MPa the gas yield varied slightly but a drastic decline was observed from 1.0 to 2.0 MPa. On the other hand, the char yield showed a clear increase at the intermediate pressure range (i.e. from 0.1 to 1.0 MPa) being the effect of pressure less evident in the range from 1.0 to 2.0 MPa. As cited in the literature, the increment of pressure favors the formation of char as a consequence of increasing the residence time of the vapors within the hot solid particle (Antal and Grønli, 2003). Additionally, volatile yields dropped as a result of physical suppression of their release (Kandiyoti et al., 2006). As observed in Table 2, the liquid fraction yield suffered a reduction with pressure from 0.1 to 1.0 MPa to remain nearly constant at higher pressures (1.0 to 2.0 MPa).

Regarding the influence of temperature, higher gas yields were obtained at 450 °C in comparison to those obtained at equivalent pressure and 350 °C. Char yields obtained at 450 °C were lower (about 10%) than those obtained at 350 °C. This char decrease with pyrolysis temperature has been well established in the literature (Antal and Grønli, 2003; Asadullah et al., 2010; Veksha et al., 2014), and related to further decomposition of biomass components. The yield of liquid products increased with temperature although to a lesser extent as pyrolysis pressure rose. The highest yield of char (ca. 45%) was obtained at 350 °C and 2.0 MPa. Under these conditions the liquid product comprised half the products (53%) and the permanent gases yielded only 3%.

3.1.2. Gas composition

The yields of the permanent gases (dry basis) collected during the pyrolysis experiments are presented in Fig. 1. In all the cases the main gas compounds were CO_2 and CO – originated from the primary decomposition of biomass (Basu, 2010; Neves et al., 2011) – followed by CH_4 and C_2 hydrocarbons. An increasing pressure reduced the formation of permanent gases. In this regard, there was a remarkable drop of CH_4 with pressure at both studied temperatures. Similar reductions, although not that pronounced, were observed for the main gas species. Temperature increased the formation of all the gaseous products, in particular CH_4 (more than 12 times) and less significantly CO, CO_2 and hydrocarbons (C_2, C_3). The highest gas yields were found at 450 °C and 1.0 MPa even though at the atmospheric pressure the results were rather close.

3.2. Char characterization

3.2.1. Proximate analysis

The proximate analysis of the chars, shown in Table 3, indicated that chars were mainly composed of fixed carbon (40–60%) and volatile matter (36–56%), with low contents of moisture (1–4%) and ash (1–2%). These results revealed the impact of pyrolysis pressure, which affected positively to char formation increasing the content of fixed carbon. Higher pyrolysis temperatures led to a reduction in the volatile matter together with an increase of fixed carbon, being this last effect usually enhanced at higher pressures. In comparison to the parent biomass (Table 1), the pyrolysis chars contained, as expected, higher levels of fixed carbon and ash, and lower moisture and volatile matter.

3.2.2. Ultimate analysis

The ultimate analysis of chars (Table 3) showed a clear increment in carbon content from 47.2% in the fresh biomass to 72–80%, together with a decrease in oxygen and hydrogen content (from 46 to 15–22% and 6 to 4–5% respectively), and a slight drop in sulfur and nitrogen. In general, the higher the temperature the higher the C content and the lower the O and H contents in the produced chars. On the other hand, increasing pressures provoked a rise in the contents of C and H and a drop in O.

The O/C and H/C ratios for the chars produced at 350 °C were about 0.22 and 0.84 respectively, while both ratios decreased to 0.16 and 0.62 when chars were prepared at 450 °C. Higher pyrolysis temperatures diminished the H/C ratio due to the enrichment in carbon on the charred material and the release of hydrogen through the volatile products and moisture. Increasing the pressure hardly affected the H/C ratio but it exerted some influence on the O/C ratio (more relevant from 0.1 to 1.0 MPa).

The minor components analyzed by ionic chromatography (F, Cl, and P) tended to accumulate in the charred solid, and their content decreased both with pyrolysis pressure and temperature. This

Table 2
Product yields of pyrolysis experiments.

Temperature (°C)	350			450		
Pressure (MPa)	0.1	1.0	2.0	0.1	1.0	2.0
Gas	9.2 ± 0.1	8.3 ± 0.4	2.8 ± 0.2	13.2 ± 0.5	13.7 ± 0.3	9.3 ± 0.3
Liquids	56.7 ± 0.1	48.6 ± 1.0	52.3 ± 0.6	61.4 ± 0.9	53.3 ± 0.1	54.9 ± 0.7
Char	34.1 ± 0.1	43.1 ± 0.6	45.0 ± 0.5	25.5 ± 0.4	33.1 ± 0.2	35.7 ± 0.4

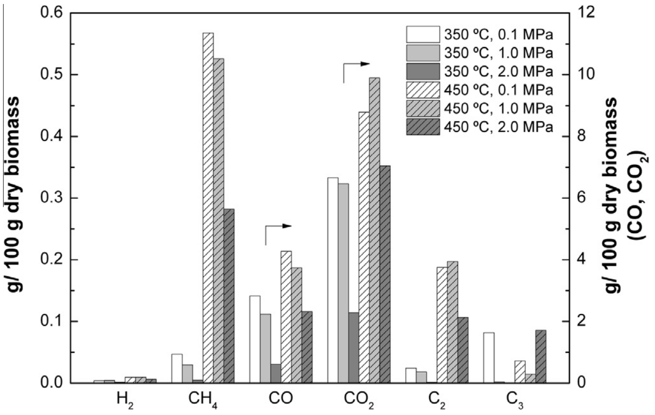

Fig. 1. Yields of permanent gases collected during the pyrolysis experiments.

drop was more noticeable for Cl while the content of P was the least influenced by these variables.

3.2.3. Heating value

Table 3 also displays the lower heating value of the chars, which increased with the severity of the pyrolytic treatment; both temperature and pressure showed a positive effect on the char heating value. As expected, the loss of moisture and light oxygenated compounds improved the feedstock heating value (Berrueco et al., 2014b). The rise in energy content of chars obtained at atmospheric pressure in comparison to the raw biomass was about a 44% (350 °C, 0.1 MPa) and a 56% (450 °C, 0.1 MPa). The operation under pressure enhanced even more the heating value of the char; from atmospheric pressure to 2.0 MPa an increment of 9% and 5% for chars prepared at 350 and 450 °C, respectively, was reported. It is worth noticing that the energy yield (Table 3)-fraction of the energy content of the raw biomass conserved in the char-varied from 50% to 70% at 350 °C and from 40% to 59% for chars prepared at 450 °C. These results were in agreement with previous studies (Xiao et al., 2010) that clearly indicated an improvement in the energy content of the material with the pyrolysis pre-treatment.

3.2.4. Surface and porosity analysis

Textural properties of the carbonaceous solids were evaluated from the analysis of CO_2 adsorption isotherms measured at 0 °C. Considering that the pyrolysis treatments were performed at low heating rates and final temperature below 500 °C, chars were expected to present mainly a microporous structure (<2 nm) (Burhenne et al., 2013). N_2 adsorption for porosity analysis is not recommended when materials present mainly micropores, due to slow diffusion of nitrogen molecules into the pores. This slow diffusion usually leads to time-consuming measurements and may cause under-equilibration of isotherms, resulting in inaccurate results (Jagiello and Thommes, 2004; Lozano-Castelló et al., 2004).

The isotherms depicted in Fig. 2 presented the typical shape of isotherms of Type I, according to the IUPAC classification, which are often associated with microporous materials.

Table 4 gathers the results of specific surface area, pore volume and average pore diameter (calculated by the Dubinin–Radushkevich method) for the chars obtained at different temperatures and pressures. The results suggested that the specific surface area was clearly affected by pyrolysis temperature and pressure. Surface areas of chars generated at the lowest temperature rose with increasing pressure, presumably due to the formation of micropores in the charred solid. The observed increase in surface area was approximately of 70% from 0.1 to 2.0 MPa. On the other hand, the pyrolysis pressure presented the opposite effect for the chars prepared at 450 °C; the specific surface areas became gradually smaller as pressure rose. Notice that despite the effect of pressure, the specific surface areas of chars obtained at 450 °C were always larger than those of chars generated at 350 °C in all cases. The evolution of specific surface area of the chars prepared at 450 °C could be related to a slight structural ordering, micropore coalescence and the formation of secondary char from the tar deposition clogging the pores under these pyrolysis conditions (Guerrero et al., 2008; Lu et al., 2002; Melligan et al., 2011). The pore volume values presented similar trends to those observed for the specific surface area. These trends may corroborate the increasing porosity of chars generated at the lowest temperature (350 °C) through the formation of a larger amount of smaller pores (increasing pore volume and decreasing of average pore size as pressure increases). On the other hand, the evolution of pore volume with pyrolysis pressure of the chars obtained at 450 °C may denote the occlusion of the smaller pores due to the deposition of secondary char, leading to slightly smaller pore volumes and larger average pore size (Melligan et al., 2011).

The results obtained for the textural properties were in qualitative agreement with previous studies. A recent work conducted by

Table 3
Yield, composition and heating value of the produced chars (as received basis).

	Temperature (°C)	350			450		
	Pressure (MPa)	0.1	1.0	2.0	0.1	1.0	2.0
Pyrolysis yields (wt.%)	Char	34.1 ± 0.1	43.1 ± 0.6	45.0 ± 0.5	25.5 ± 0.4	33.1 ± 0.2	35.7 ± 0.4
Proximate analysis (wt.%)	Moisture	2.43 ± 0.03	1.42 ± 0.10	1.72 ± 0.17	4.76 ± 0.40	3.32 ± 0.43	3.56 ± 0.25
	Volatiles	56.4 ± 2.3	54.5 ± 0.01	55.0 ± 1.5	40.8 ± 1.6	36.9 ± 1.2	35.9 ± 1.4
	Fixed carbon	40.7 ± 2.9	42.4 ± 0.2	43.3 ± 1.2	52.9 ± 1.2	58.6 ± 1.5	59.8 ± 1.8
	Ash	1.15 ± 0.44	1.4 ± 0.5	1.0 ± 0.2	1.88 ± 0.7	1.69 ± 0.13	1.83 ± 0.29
Ultimate analysis (wt.%)	C	71.6 ± 0.4	72.6 ± 0.6	73.6 ± 0.1	75.7 ± 0.1	78.5 ± 0.9	78.0 ± 0.1
	H	5.05 ± 0.09	20.9 ± 0.6	20.2 ± 0.1	18.5 ± 0.1	15.7 ± 0.9	16.1 ± 0.2
	N	0.35 ± 0.11	0.32 ± 0.09	0.32 ± 0.08	0.32 ± 0.09	0.34 ± 0.09	0.31 ± 0.09
	S	0.02 ± 0.015	0.01 ± 0.002	0.01 ± 0.001	0.01 ± 0.001	0.01 ± 0.001	0.01 ± 0.001
	O*	21.9 ± 0.4	20.2 ± 1.2	20.0 ± 0.1	18.15 ± 0.04	15.5 ± 0.9	15.8 ± 0.1
	F	0.002 ± 0.0008	0.0022 ± 0.0001	0.0014 ± 0.0001	0.0022 ± 0.0001	0.0013 ± 0.0001	0.0027 ± 0.0007
	Cl	0.0859 ± 0.0303	0.0586 ± 0.0001	0.0206 ± 0.0002	0.0509 ± 0.0084	0.021 ± 0.001	0.0319 ± 0.0026
	P	0.0147 ± 0.0046	0.0077 ± 0.0004	0.0077 ± 0.0004	0.0114 ± 0.0018	0.0055 ± 0.002	0.0067 ± 0.0031
	H/C	0.85 ± 0.02	0.84 ± 0.021	0.84 ± 0.01	0.62 ± 0.012	0.61 ± 0.024	0.62 ± 0.01
	O/C	0.23 ± 0.005	0.21 ± 0.007	0.2 ± 0.001	0.18 ± 0.001	0.15 ± 0.01	0.15 ± 0.002
Lower heating value (MJ/kg)	LHV	25.56 ± 0.11	26.8 ± 0.07	27.87 ± 0.07	27.76 ± 0.08	28.76 ± 0.24	29.22 ± 0.06
Carbon yield (wt.%)		51.7 ± 0.4	66.3 ± 1.1	70.2 ± 0.8	40.9 ± 0.7	55.0 ± 0.8	59.0 ± 0.7
Energy yield$_{LHV}$ (%)		49.1 ± 0.4	65.1 ± 1.0	70.7 ± 0.9	39.9 ± 0.7	53.7 ± 0.6	58.8 ± 0.7

* By difference.

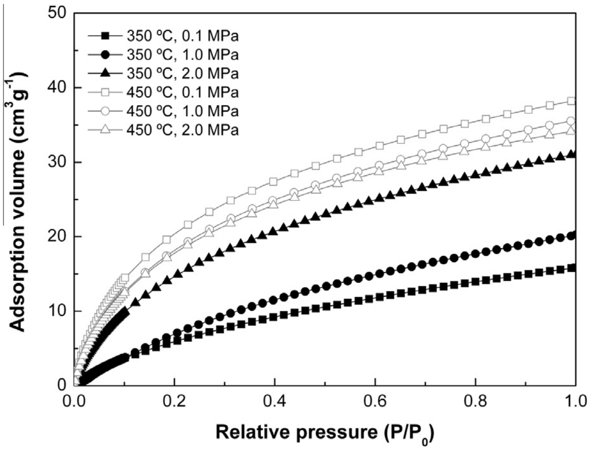

Fig. 2. CO_2 adsorption isotherms of the char samples at different experimental conditions.

López et al. (2013) reported on wood chars produced at 600 °C with microporous structures (1.62–0.81 nm) and specific surface areas in the range of 168–374 $m^2\,g^{-1}$ measured by N_2 adsorption. Additionally, Guerrero et al. (2008), produced chars from eucalyptus at low heating rates and final temperatures from 600 to 800 °C that presented high specific surface areas of ca. 580 $m^2\,g^{-1}$ and low micropore volumes (0.2 $cm^3\,g^{-1}$), calculated with the DR method from CO_2 adsorption isotherms.

3.2.5. Structural analysis

Scanning Electronic Microscopy (SEM) measurements were carried out to characterize the biomass and char samples (images not shown). The raw biomass presented the typical lignocellulosic structure made of solid cells in the form of plats with some little slits on the surface (Apaydin-Varol and Pütün, 2012), overall it displayed a solid material with non-visible pores. From a qualitative point of view, the charred solids prepared at 350 °C preserved similar structures with minor changes; at some points small round pores were detected. The chars prepared at 450 °C developed a more fibrous-like texture, as compared to those obtained at 350 °C, but negligible variations among samples produced at different pyrolysis pressure could be observed. In general the chars tended to retain the morphology of the original lignocellulosic structure, this fact was observed even at 550 °C by Apaydin-Varol and Pütün (2012). At a first sight, it seemed that temperature broke the outer surface structure resulting in slits and canal-like crevices.

Regarding the influence of pyrolysis pressure on the char produced at 450 °C, it is worth noting that the formation of round pores was more frequent at atmospheric pressure, probably because of the ease escape of volatiles. Moreover, it can be pointed out the presence of a larger amount of solid deposited on the char surface as pressure was increased, presumably due to the formation of secondary char from the tar repolymerization (Asadullah et al., 2010; Melligan et al., 2011). These results were in agreement with the evolution of specific surface areas discussed in the textural analysis section.

Table 4
Porosity results (Dubinin–Radushkevich method).

Temperature (°C)	350			450		
Pressure (MPa)	0.1	1.0	2.0	0.1	1.0	2.0
Surface area ($m^2\,g^{-1}$)	199	230	343	429	419	385
Pore volume ($cm^3\,g^{-1}$)	0.07	0.08	0.14	0.14	0.14	0.13
Pore size (nm)	0.97	0.92	0.91	0.83	0.86	0.84

3.2.6. Reactivity

The oxidation reactivity of the char samples was determined from their isothermal mass loss curves under an O_2–N_2 atmosphere at 320 °C, 350 °C and 450 °C. Fig. 3 shows the conversion profile at 450 °C of the chars prepared at the different combinations of pyrolysis pressure and temperature. It can be noticed that the conversion rate decreased with the pyrolysis pressure in the interval from 0.1 to 1.0 MPa, while this influence was less evident in the range 1.0 to 2.0 MPa. The pyrolysis pressure considerably affected the conversion rate for the chars prepared at 450 °C, but the influence was minor for the chars obtained at the lowest pyrolysis temperature (350 °C). Regarding the effect of pyrolysis temperature on the conversion rate, it may be concluded that the char preparation temperature presented an opposite effect on the char conversion rate. This effect was more relevant as pyrolysis pressure increased.

The random pore model (RPM) (Bhatia and Perlmutter, 1980; Everson et al., 2011) was applied to estimate the conversion rates of the chars in an oxygen atmosphere. This model incorporates some features as pore size distribution, pore growth and coalescence, all of which can be related to the initial properties of the chars, and has been proven to be adequate for modeling the gasification of both coal and biomass chars (Everson et al., 2011; Lin and Strand, 2013; Matsumoto et al., 2009).

By using the random pore model the overall reaction oxidation rate of char can be expressed as:

$$\frac{dX}{dt} = K_p(1-X)\sqrt{1-\psi\ln(1-X)} \qquad (1)$$

where K_P and ψ are the kinetic constant and the pore structure parameter of the random pore model, respectively.After integration:

$$\frac{2}{\psi}\left[\sqrt{1-\psi\ln(1-X)-1}\right] = K_p t \qquad (2)$$

The structural parameter ψ, related to the pore structure in the initial char sample, was determined using the regression developed by Everson and co-workers based on the definition of the reduced time (Everson et al., 2008). At a given conversion, the reduced time is only ψ dependent, being independent from other reaction conditions (temperature, oxidation agent, etc.). As shown in Eq. (3), in our case, the reduced time was defined as $t_X/t_{0.8}$ to avoid uncertainties at high conversions (Lin and Strand, 2013).

$$\frac{t_X}{t_{0.8}} = \frac{\sqrt{1-\psi\ln(1-X)}-1}{\sqrt{1-\psi\ln(1-0.8)}-1} \qquad (3)$$

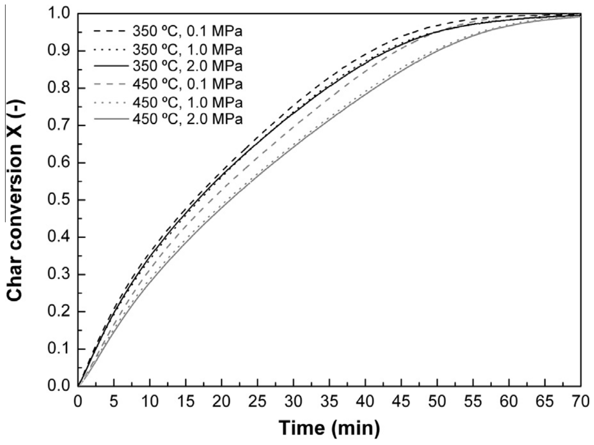

Fig. 3. Conversion profiles (450 °C/5 vol.% O_2 atmosphere) of chars prepared at different pyrolysis pressures and temperatures.

3.2.7. Determination of model parameters

As stated previously, the structural parameter ψ was determined using the reduced time ($t_X/t_{0.8}$). A least square method was applied to minimize the following expression:

$$\sum_{x=0}^{x=1}\left|\frac{t_X}{t_{0.8}}-\frac{\sqrt{1-\psi\ln(1-X)}-1}{\sqrt{1-\psi\ln(1-0.8)}-1}\right| \qquad (4)$$

Fig. 4 shows the ψ values for the different chars evaluated in the present study. The different values obtained for ψ implied that the pyrolysis conditions influenced the char structures. According to the definition of the parameter ψ, for similar pores (length and diameter), higher surface areas would lead to lower values of ψ. Very low values of ψ are usually related to high porosity, and therefore with a negligible pore growth during the reaction (Bhatia and Perlmutter, 1980; Everson et al., 2008). The values of the parameter ψ for the prepared chars suggested that the chars produced at lower temperature presented increasing porosity with the pyrolysis pressure (Lin and Strand, 2013). The effect was the opposite for the chars obtained at 450 °C. Another important point worth mentioning is the lower value of the ψ parameter for all the chars obtained at 350 °C, when compared to their 450 °C counterparts. This fact could be related to smaller pore sizes and little pore growth during the oxidation reaction (i.e. a larger extent of reaction on the particle surface).

Once the ψ values were determined, the reaction rate constants, K_P, could be calculated according to Eq. (2). The linear fit for the calculation of K_P (not shown) confirmed the validity of the random pore model used in the intrinsic rate equation. The same procedure was used to determine the reaction rate constants for all the char samples (Lin and Strand, 2013). Fig. 4 presents the values of K_P obtained at a constant oxidation temperature of 450 °C following the procedure explained in the experimental section for char reactivity. The main features that could be extracted from the obtained K_P data were the higher values obtained for the chars prepared at 350 °C, which denoted a higher reactivity of the chars prepared at lower temperature, and the clear decrease on the value of K_P with pressure for the chars obtained at 450 °C (this drop was negligible at 350 °C). The lower K_P values for the chars obtained at 450 °C in comparison to those obtained at 350 °C indicated a lower reactivity of the chars obtained at higher temperature. This might be related to the deposition of secondary char on the char surfaces through the secondary reactions of the evolving tars (tar repolymerization reactions).

The dependence of the reaction rate on temperature for each one of the prepared chars was obtained using Arrhenius plots (Fig. 5). Notice that the reactivity tests were carried out at least three times at each studied temperature (320, 350 and 450 °C) in order to obtain significant average values.

The results in Fig. 5 and Table 5 show that chars prepared at 350 °C and different pressures presented very similar oxidation kinetic parameters, and therefore analogous reactivity under air atmosphere. Regarding the influence of pyrolysis temperature on the char reactivity, it can be noticed that the chars prepared at 450 °C presented much higher activation energies (96.6–98.6 kJ mol^{-1}) than those prepared at 350 °C (64.8–64.9 kJ mol^{-1}), denoting a lower reactivity. Fig. 5 also showed the influence of pyrolysis pressure on K_P. The value of K_P decreased as the pyrolysis pressure increased, being this effect more notorious in the range from 0.1 to 1.0 MPa. Only minor differences were noticed between the K_P values of the chars obtained at 1.0 and 2.0 MPa.

The activation energies of the combustion reaction obtained in the current study are in agreement with the findings of previous studies on the oxidation of chars prepared under slow pyrolysis, modeled as one-step global reaction. These works reported activation energies from 71 to 142 kJ mol^{-1}, for a variety of biomasses and pyrolysis temperatures (Adánez et al., 2001; Di Blasi, 2009).

3.2.8. Relation between char reactivity and physical properties of char

The results presented in the current work indicated that the structural characteristics and the reactivity of the chars were clearly dependent on the pyrolysis conditions. The results showed that at the lowest studied temperature (350 °C), biomass decomposition took place to a lower extent than at 450 °C, and the reorganization of the chemical bonds led to a less organized, more oxygenated structure that presented higher reactivity. Furthermore, as pyrolysis temperature rose it was observed an increase in the formation of secondary char. This secondary char is a coke derived from the cracking and repolymerization of the tar produced in the primary pyrolysis of biomass, which deposits on the surface of the hot carbonaceous solid. This more aromatic and less reactive secondary char affected the pore structure of the produced chars and their overall reactivity (Antal and Grønli, 2003). The larger production of secondary char at higher temperature could be related to the increasing rate of tar repolymerization reactions with temperature. Pressure also affected the tar repolymerization reactions: this phenomenon was attributed to a higher boiling point and a smaller specific volume of the tar compounds, which increased their intra and interparticle residence time and the extent of decomposition/repolymerization as they escaped from the biomass particles and went through the biomass bed (Berrueco et al., 2014a; Kandiyoti et al., 2006). This last effect was clearly observed in the chars obtained at 450 °C, which

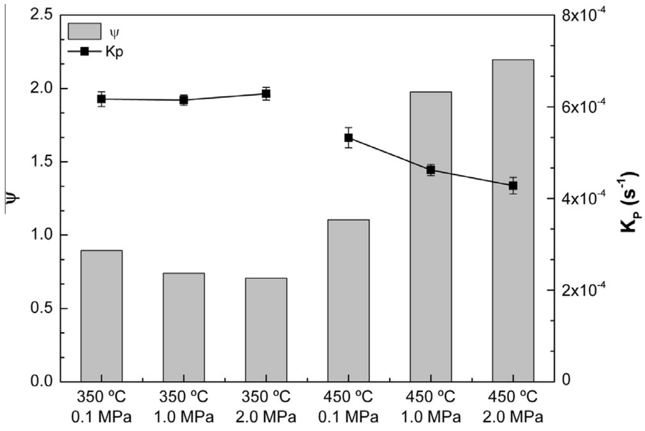

Fig. 4. ψ and K_P (450 °C) for chars produced at different temperatures (350 and 450 °C) and pressures (0.1, 1.0 and 2.0 MPa).

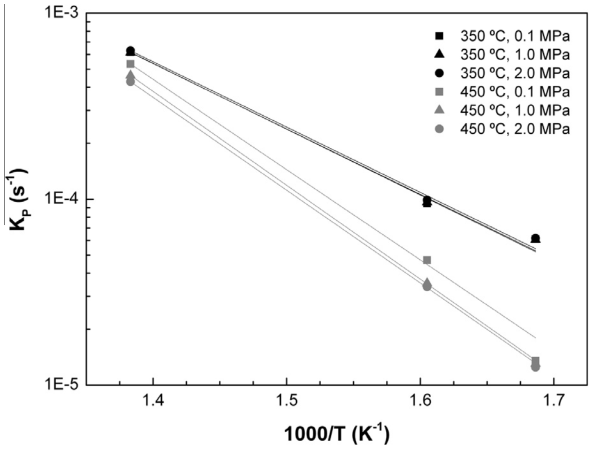

Fig. 5. Arrhenius plot of K_P of prepared chars in the temperature range 320–450 °C.

Table 5
Char oxidation kinetic parameters for random pore model rate equation.

Temperature (°C)	Pressure (MPa)	Apparent pre-exponential factor A_0 (s^{-1})	Activation energy, E_A ($kJ\ mol^{-1}$)
350	0.1	29.18	64.89
350	1.0	28.83	64.81
350	2.0	29.69	64.84
450	0.1	7398.10	98.61
450	1.0	5194.01	97.53
450	2.0	4102.04	96.61

presented lower specific surface areas as pressure increased. This fact suggested the occlusion of the smaller pores due to the deposition of secondary char at 450 °C, a phenomenon not observed for the char generated at 350 °C, where secondary char formation could be less significant. All these trends concerning char structure were in good agreement with their oxidation reactivity and the calculated parameters of the random pore model. On the one hand, the evolution of the parameter ψ suggested similar trends to those inferred from the specific surface area: increasing porosity with pyrolysis pressure for the chars obtained at 350 °C and the opposite effect for the chars obtained at 450 °C. The oxidation kinetic parameters (K_P) of the chars prepared at 350 °C presented very similar values, and therefore similar reactivity, whereas the chars prepared at 450 °C showed lower reactivity in comparison to those obtained at 350 °C and decreasing reactivity with pyrolysis pressure. The observed trends on K_P with pressure and temperature confirmed the phenomena related to char production involving the rearrangement of char structures and the formation of secondary char previously explained. Additionally, the results presented here indicated that the temperature interval from 350 to 450 °C might be crucial in this mechanism of tar repolymerization.

4. Conclusions

This study provides insight into the influence of pyrolysis pressure on the properties of chars obtained at relatively low temperatures.

Both char porosity and reactivity are the consequence of pyrolysis conditions and the formation of secondary char by cracking and repolymerization of tars. The extension of these phenomena becomes more important at high pressures, provoking a decrease on surface area of the chars produced at 450 °C, a fact not observed for the chars obtained at 350 °C.

The information attained herein is of great interest for the design of new gasification concepts or the development of bioenergy carriers.

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